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## (54) PROCESS FOR PREPARING CHLORINATED HYDROCARBONS

5 (71) Wc, SUMITOMO CHEMICAL COMPANY, LIMITED, a Japanese Company, of No. 15, Kitahama 5-Chome, Higashiku, Osaka-Shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

10 This invention relates to a process for preparing chlorinated hydrocarbons by oxychlorination. More specifically, the invention relates to a process for preparing chlorinated hydrocarbons and/or highly chlorinated hydrocarbons by oxychlorination of hydrocarbons and/or of partially chlorinated hydrocarbons respectively (for brevity these may be referred to hereinafter as "starting hydrocarbons"), in which the oxychlorination is carried out using 15 a molten salt catalyst.

15 It has previously been known (for example, as disclosed in United States Patent Specification No. 3,557,229), to use a molten salt catalyst comprising a copper chloride for the production of chlorinated hydrocarbons such as monochloroethylene, 1,2-dichlorethane or monochloroethane by oxychlorination of aliphatic hydrocarbons. However, the molten salt catalyst used in the U.S. Patent Specification 20 has low activity, and cannot yield highly chlorinated hydrocarbons, such as tetrachloromethane, trichloroethylene or tetrachloroethylene, as main products. Furthermore, the conversions of the starting hydrocarbons to 25 chlorinated hydrocarbons are low; and the use of such a molten salt catalyst also has the disadvantage that combustion of very large quan-

tities of the starting hydrocarbons occurs, causing an extremely great loss thereof.

30 In view of this situation, we have sought molten salt catalysts for the production of chlorinated hydrocarbons from hydrocarbons and/or partially chlorinated products thereof by oxychlorination and which are free from the above-described disadvantages.

35 According to the present invention, there is provided a process for preparing chlorinated hydrocarbons comprising oxychlorinating a starting hydrocarbon as herein defined with oxygen and chlorine and/or hydrogen chloride by contacting the reactants with a molten salt catalyst at a temperature of from 250 to 650°C, said catalyst comprising the following components to a total of 100%: (1) from 95 to 50 mole % of copper chloride as herein defined or a mixture of copper chloride and of an alkali metal chloride and/or an alkaline earth metal chloride, and (2) from 5 to 50 mole % of at least one chloride of a metal selected from iron, manganese, chromium, nickel, palladium and the rare earth metals. By a starting hydrocarbon we mean herein a hydrocarbon, a partially chlorinated hydrocarbon, or mixtures of said hydrocarbon and said partially chlorinated hydrocarbon.

40 The process of this invention can be applied very effectively to the production of partially chlorinated hydrocarbons such as monochloromethane, monochloroethylene, 1,2-dichloroethane, monochloroethane, monochloropropylene, monochlorobenzene or dichlorobenzene, and highly chlorinated hydrocarbons having at 45 least one carbon atom per molecule to which at least two chlorine atoms are bonded, such as

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- trichloromethane, tetrachloromethane, trichloroethylene, tetrachloroethylene or trichloroethane.
- The molten salt catalyst used in this invention comprises (1) copper chloride (this term is used in this specification to include both cupric and cuprous chloride) or a mixture of a copper chloride and an alkali metal chloride and/or an alkaline earth metal chloride and (2) at least one chloride of a metal selected from iron, manganese, chromium, nickel, palladium and the rare earth metals.
- The chloride (1) and the chloride (2) are used as a mixture of 95 to 50 mole % of (1) and 5 to 50 mole % of (2), preferably as a mixture of 93 to 60 mole % of (1) and 7 to 40 mole % of (2). When the proportion of the chloride (2) is less than 5 mole %, the resulting catalyst becomes unsatisfactory: if the chloride (2) is a chloride of iron, manganese, chromium, or nickel, the catalyst has low selectivity to highly chlorinated hydrocarbons; and if the chloride (2) is a chloride of palladium or a rare earth metal, the decomposition of the starting hydrocarbon occurs principally, resulting in a decrease in the yield of the chlorinated hydrocarbon. On the other hand, if the proportion of the chloride (2) exceeds 50 mole %, the molten salt is lost by volatilization, and, moreover, an economic disadvantage results because of the need for a great quantity of expensive salt.
- As the chloride (1), there may be used copper chloride or a mixture of copper chloride and an alkali metal chloride and/or alkaline earth metal chloride. The alkali metal chloride is preferably lithium chloride, sodium chloride, or potassium chloride, and as the alkaline earth metal chloride, magnesium chloride is preferred. The alkali metal chloride and/or alkaline earth metal chloride are used mainly to lower the melting point of the molten salt catalyst. Usually, not more than 2 moles, preferably not more than 1 mole, of the alkali metal chloride and/or the alkaline earth metal chloride is used per mole of the copper chloride.
- Examples of the chloride (2) are iron chloride, manganese chloride, chromium chloride, nickel chloride, palladium chloride, lanthanum chloride, cerium chloride, praseodymium chloride, and neodymium chloride, which may be used either alone or as a mixture of two or more thereof.
- When a molten salt comprising the chloride (1) and less than 5 mole % of the chloride (2), for example neodymium chloride, is used as a catalyst, a recombination reaction occurs and the catalyst is not effective for the production of chlorinated hydrocarbons. However, if a chloride of (2) is further added thereto to adjust the proportion of the chlorides (2) in total to 5 mole % or more, the molten salt can be a very effective catalyst for oxychlorination of hydrocarbons.
- A further requirement of the molten salt catalyst used in the present invention is that it should have a melting point of not more than 650°C.
- The starting hydrocarbons used in this invention include, for example, aliphatic hydrocarbons having 1 to 4 carbon atoms such as methane, ethane, ethylene, propane, propylene, n-butane, n-butylene, isobutane, iso-butylene, and butadiene; and partially chlorinated products of said hydrocarbons such as monochloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane or 1,4-dichlorobutane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, naphthalene or anthracene; and partially chlorinated products of these aromatic hydrocarbons. Of course, it is possible to obtain highly chlorinated hydrocarbons by recycling the partially chlorinated hydrocarbons obtained by the process of this invention.
- The starting hydrocarbon can be fed either as a gas or a liquid or also as a mixture with a diluent. The chlorine source used for oxychlorination may be hydrogen chloride, chlorine or a mixture thereof.
- As the oxygen source, not only oxygen alone but also air or a mixture of oxygen and an inert gas, preferably air, may be used.
- In performing the process of this invention, the ratio of the starting hydrocarbon, chlorine source and oxygen to be fed is not particularly restricted, but is determined according to the starting hydrocarbon and the desired chlorinated hydrocarbon. Generally, the chlorine source is used in a ratio of 0.1 to 20 mole, as chlorine ( $Cl_2$ ), per mole of the starting hydrocarbon. When chlorine is used as the chlorine source, 0.05 to 2 mole of oxygen is preferably used per mole of chlorine, and when hydrogen chloride is used as the chlorine source, 0.05 to 2 mole of oxygen is preferably used per mole of hydrogen chloride.
- The catalyst is used in the molten state held at a temperature of 250 to 650°C, preferably 300 to 600°C. When the temperature of the molten salt catalyst is below 250°C, the conversion of the starting hydrocarbon becomes extremely low. If the temperature of the molten salt catalyst exceeds 650°C, the starting hydrocarbon undergoes decomposition, and great quantities of it are lost. The molten salt catalyst used in this invention also includes a catalyst system which is not in the molten state throughout the entire temperature range of from 250 to 650°C. For example, for a catalyst having a melting point of 400°C, the reaction is carried out at 400 to 650°C.
- The reaction pressure used in performing the process of this invention is not particularly restricted, but generally the reaction is performed at 0 to 30 Kg/cm<sup>2</sup> gauge.
- The residence time in the process of this invention varies somewhat according to the reaction temperature, the mole ratio of the

starting materials, the type of the catalyst system and the desired product. Generally, a residence time of from a fraction of a second to 60 seconds is sufficient.

The oxychlorination of the starting hydrocarbon can be performed conveniently by blowing the starting hydrocarbon into the molten salt catalyst described above or passing it over the surface of the molten salt catalyst. In short, it is only necessary to bring the starting hydrocarbon to be oxychlorinated into contact with the molten salt catalyst.

However, if the starting hydrocarbon and oxygen are fed into the molten salt catalyst in the form of a mixture, a combustion reaction occurs to cause a loss of the starting hydrocarbon. Therefore it is usually preferred that the starting hydrocarbon, the chlorine source and oxygen should be fed separately, or the starting hydrocarbon and the chlorine source, or the chlorine source and oxygen, should each be fed as a mixture. Preferably, the reaction is carried out by introducing the starting hydrocarbon, chlorine source and oxygen into one reactor; or a chlorinating reactor for the starting hydrocarbon and an oxidizing reactor for the molten salt catalyst are provided separately, and the molten salt catalyst in both of these reactors is circulated. In the latter type of reaction, the starting hydrocarbon alone or a mixture of it with the chlorine source is fed into the former reactor, and oxygen or a mixture of it with the chlorine source is fed into the latter reactor. However, the reaction in accordance with the process of this invention is not limited to these illustrated types.

The process of this invention described in detail above makes it possible to prepare chlorinated hydrocarbons, especially highly chlorinated hydrocarbons such as trichloromethane, tetrachloromethane, trichloroethylene, tetrachloroethylene or trichloroethane, in high yields as compared with the preparation of chlorinated hydrocarbons by oxychlorination of hydrocarbons and/or partially chlorinated products thereof using the known molten salt catalyst, and it has very great commercial significance.

Furthermore, the molten salt catalyst used in this invention has a very high chlorinating ability for hydrocarbons as compared with the conventional molten salt catalyst, and the combustion of the starting hydrocarbons does not occur easily. The use of the molten salt catalyst in the present invention has the advantage that it considerably reduces the formation of oxidation by-products of the starting hydrocarbons in comparison with the conventional method of producing chlorinated hydrocarbons by oxychlorination using a catalyst supported on a carrier and can increase the conversion of the starting hydrocarbons to highly chlorinated hydrocarbons. In addition, the reaction of this invention is very easy to control.

The present invention will be illustrated in greater detail below by reference to the Examples, which are for the purpose of illustration and are not in any way intended to limit the present invention, and to Comparative Examples.

#### Example 1.

A "Pyrex"\*\* glass reactor having an inner diameter of 60 mm and a height of 500 mm and equipped with two glass blow pipes (liquid depth 10 cm) was charged with 339 cc of a molten salt composed of 15 mole % of ferric chloride and 85 mole %, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chlorides to potassium chloride being 7 : 3. The molten salt was heated and maintained at 480°C. Into the molten salt were fed 100 cc/min. of ethylene from one blow pipe, and 100 cc/min. of hydrogen chloride and 125 cc/min. of air from the other blow pipe. The oxychlorination reaction of ethylene was performed continuously for 40 minutes. The effluent gas from the reactor was cooled to -30°C. The reaction product was collected and analyzed using gas-chromatography (The same analytical method was used in all of the following Examples). The conversion of ethylene was 99%. The composition of the product was as shown in Table 1.

Table 1.

Product	Weight %	
Monochloroethylene	9.1	
1,2-Dichloroethane	4.3	
1,2-cis-Dichloroethylene	8.4	100
1,2-trans-Dichloroethylene	5.1	
1,1-Dichloroethylene	0.6	
Trichloroethylene	17.2	
1,1,2-Trichloroethane	1.1	
Tetrachloroethylene	54.2	105
Total	100.0	

#### Example 2.

The oxychlorination of ethylene was performed in the same way as set forth in Example 1 except that there was used a molten salt composed of 10 mole% of neodymium chloride and 90 mole%, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 7:3. The reaction product was collected and analyzed. The conversion of ethylene was about 100%, and the composition of the product was as shown in Table 2.

\* "Pyrex" is a Registered Trade Mark.

Table 2.

	<i>Product</i>	<i>Weight %</i>
5	Monochloroethylene	0.1
	1,2- <i>cis</i> -Dichloroethylene	4.3
	1,2- <i>trans</i> -Dichloroethylene	3.3
	1,2-Dichloroethane	trace
	1,1-Dichloroethylene	1.0
	Trichloroethylene	25.3
10	1,1,2-Trichloroethane	trace
	Tetrachloromethane	8.9
	Tetrachloroethylene	57.0
	Total	99.9

Example 3.

The same reactor as used in Example 1 was charged with 339 cc of a mixture of 10 mole% of manganese chloride and 90 mole% in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 6:4, and then heated and maintained at 510°C.

Into the molten salt were introduced 45 cc/min of methane from one blow pipe and 180 cc/min. of hydrogen chloride and 225 cc/min. of air from the other blow pipe, and the oxychlorination of methane was performed continuously for 40 minutes. The effluent gas from the reactor was cooled to -10°C. The reaction product was collected and analyzed. The conversion of methane was about 100%, and the composition of the product was as shown in Table 3.

Table 3.

	<i>Product</i>	<i>Weight %</i>
35	Tetrachloromethane	87.3
	Trichloroethylene	0.7
	Tetrachloroethylene	12.0
	Total	100.0

Example 4.

The oxychlorination of methane was performed by the same method as set forth in Example 3 except that a molten salt composed of 10 mole% of ferric chloride and 90 mole, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 6:4, was used, and the temperature of the molten salt was maintained at 450°C. The reaction product was collected and analyzed. The conversion of methane was 99%, and the composition of the product was as shown in Table 4.

Table 4.

55	Monochloromethane	trace
	Dichloromethane	3.2
	Trichloromethane	7.8
	Tetrachloromethane	88.0
	Trichloroethylene	trace
	Tetrachloroethylene	0.9
	Total	99.9

Example 5.

The oxychlorination of propane was performed in the same way as set forth in Example 1 except that there was used a molten salt catalyst composed of 5 mole% of magnesium chloride, 38 mole% of ferric chloride and 57 mole%, in total, of cuprous chloride and cupric chloride, and the temperature of the molten salt catalyst was maintained at 500°C. The reaction product was collected, and analyzed. The conversion of propane was about 100%, and the composition of the product was as shown in Table 5.

Table 5.

	<i>Product</i>	<i>Weight %</i>
	Monochloroethylene	trace
	1,2- <i>cis</i> -Dichloroethylene	0.1
	1,2- <i>trans</i> -Dichloroethylene	0.1
	1,1-Dichloroethylene	trace
	Tetrachloromethane	24.1
	Trichloroethylene	5.4
	Tetrachloroethylene	70.2
	Total	99.9

Example 6.

The oxychlorination of propylene was performed in the same way as set forth in Example 1 except that there was used a molten salt catalyst composed of 10 mole% of palladium chloride and 90 mole% in total of cuprous chloride and cupric chloride, and the temperature of the molten salt was maintained at 490°C. The reaction product was collected, and analyzed. The conversion of propylene was about 100%, and the composition of the product was as shown in Table 6.

Table 6.

	<i>Product</i>	<i>Weight %</i>
	Monochloroethylene	0.1
	1,2- <i>cis</i> -Dichloroethylene	0.1
	Tetrachloromethane	40.6
	Trichloroethylene	8.9
	Tetrachloroethylene	50.3
	Total	100.0

Comparative Example 1.

The procedure of Example 6 was repeated except that there was used a molten salt catalyst composed of 0.5 mole% of palladium chloride and 99.5 mole% in total of cuprous chloride and cupric chloride. The product obtained consisted of carbon, high boiling tar, CO and CO<sub>2</sub>. The formation of chlorinated hydrocarbons substantially was not observed.

Example 7.

The procedure of Example 5 was repeated except that a chlorinated hydrocarbon mixture of the composition shown in Table 7 was used as the starting hydrocarbon. The recovery was about 100%, and the composition of the product was as shown in Table 8.

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Table 7.

	<i>Starting Hydrocarbons</i>	<i>Weight %</i>
	1,2-Dichloroethane	38.0
	Tetrachloromethane	0.5
5	1,1,2-Trichloroethane	49.3
	Tetrachloroethylene	1.2
	1,4-Dichlorobutane	11.0
	Total	100.0

Table 8.

	<i>Product</i>	<i>Weight %</i>
	1,2-cis-Dichloroethylene	3.1
10	1,2-trans-Dichloroethylene	2.0
	1,1-Dichloroethylene	1.5
15	Trichloroethylene	18.5
	Tetrachloromethane	17.3
	Tetrachloroethylene	57.6
	Total	100.0

**Example 8.**

The oxychlorination of ethylene was performed in the same way as set forth in Example 1 except that there was used a molten salt catalyst composed of 15 mole% of ferric chloride, 0.5 mole% of neodymium chloride and 84.5 mole%, in total, of cuprous chloride, cupric chloride and potassium chloride, with the mole ratio of the copper chloride to potassium chloride being 7:3. The reaction product was collected, and analyzed. The conversion of ethylene was 98%, and the composition of the product was as shown in Table 9.

Table 9.

	<i>Product</i>	<i>Weight %</i>
	Monochloroethylene	0.8
35	1,2-cis-Dichloroethylene	2.9
	1,2-trans-Dichloroethylene	9.0
	1,2-Dichloroethane	0.4
	1,2-Dichloroethylene	0.6
	Tetrachloromethane	1.0
40	Trichloroethylene	31.2
	1,1,2-Trichloroethane	trace
	Tetrachloroethylene	54.1
	Total	100.0

When the above procedure was repeated using praseodymium chloride instead of neodymium chloride, almost the same product as above was obtained.

**Example 9.**

A "Pyrex" glass reactor having an inner diameter of 60 mm and a height of 800 mm and equipped with two blow pipes of glass (liquid depth 43 cm) was charged with 1272 cc of a molten salt composed of 10 mole% of ferric chloride and 90 mole%, in total of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 7:3, and the temperature of the molten salt was maintained at 330°C. The reaction product was collected, and analyzed. The conversion of ethylene was 90%, and the composition of the product was as shown in Table 12.

the molten salt was heated and maintained at 330°C. Into the molten salt were introduced 100 cc/min. of ethylene from one blow pipe and 100 cc/min. of hydrogen chloride and 125 cc/min. of air from the other blow pipe, and the oxychlorination of ethylene was performed continuously for 40 minutes. The effluent gas from the reaction tube was cooled to -30°C. The reaction product was collected and analyzed. The conversion of ethylene was 98%, and the composition of the product was as shown in Table 10.

Table 10.

<i>Product</i>	<i>Weight %</i>
Monochloroethylene	0.1
1,2-Dichloroethane	18.3
1,2-cis-Dichloroethylene	3.7
1,2-trans-Dichloroethylene	2.3
1,4 Dichlorobutane	19.8
1,1-Dichloroethylene	0.4
Trichloroethylene	6.5
1,1,2-Trichloroethane	6.0
Tetrachloroethylene	42.9
Total	100.0

**Example 10.**

The procedure of Example 1 was repeated except that there was used a molten salt catalyst composed of 9.9 mole% of manganese chloride, 1 mole% of palladium chloride and 89.1 mole%, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 6:4; and *n*-butane was used as the starting hydrocarbon. The reaction product was collected, and analyzed. The conversion of *n*-butan was about 100%, and the composition of the product was as shown in Table 11.

Table 11.

<i>Product</i>	<i>Weight %</i>
Tetrachloromethane	9.2
Trichloroethylene	3.3
Tetrachloroethylene	9.0
Hexachlorobutadiene	78.5
Total	100.0

**Example 11.**

The oxychlorination of ethylene was performed in the same way as set forth in Example 1 except that there was used a molten salt composed of 10 mole% of ferric chloride and 90 mole, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 7:3, and the temperature of the molten salt was maintained at 330°C. The reaction product was collected, and analyzed. The conversion of ethylene was 90%, and the composition of the product was as shown in Table 12.

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Table 12.

	<i>Product</i>	<i>Weight %</i>
5	Monochloroethylene	7.5
	Monochloroethane	0.1
	1,2- <i>cis</i> -Dichloroethylene	2.6
	1,2- <i>trans</i> -Dichloroethylene	0.4
	1,2-Dichloroethane	70.5
	1,1-Dichloroethylene	0.4
10	Trichloroethylene	4.6
	1,1,2-Trichloroethane	2.0
	Tetrachloroethylene	11.9
	Total	100.0

## Comparative Example 2.

The oxychlorination of ethylene was performed in the same way as set forth in Example 1 except that there was used a molten salt catalyst composed of 70 mole%, in total, of cuprous chloride and cupric chloride and 30 mole% of potassium chloride. The reaction product was collected, and analyzed. The conversion of ethylene was 55%, and the composition of the product was as shown in Table 13.

	Table 13.	
25	Monochloroethylene	35.2
	1,2- <i>cis</i> -Dichloroethylene	4.4
	1,2- <i>trans</i> -Dichloroethylene	7.1
	1,2-Dichloroethane	13.2
	1,1-Dichloroethylene	0.7
	Trichloroethylene	5.8
30	1,1,2-Trichloroethane	2.5
	Tetrachloroethylene	22.6
	CO, CO <sub>2</sub>	8.5
	Total	100.0

## Comparative Example 3.

The oxychlorination of ethylene was performed in the same way as set forth in Example 11 except that there was used a molten salt catalyst composed of 70 mole%, in total, of cuprous chloride and cupric chloride and 30 mole% of potassium chloride. The reaction product was collected, and analyzed. The conversion of ethylene was found to be 20%, and the composition of the product was as shown in Table 14.

	Table 14.	
	<i>Product</i>	<i>Weight %</i>
50	Monochloroethylene	1.8
	Monochloroethane	trace
	1,2- <i>cis</i> -Dichloroethylene	1.3
	1,2- <i>trans</i> -Dichloroethylene	0.5
	1,2-Dichloroethane	76.3
	1,1-Dichloroethylene	0.3
55	Trichloroethylene	4.8
	1,1,2-Trichloroethane	0.7
	Tetrachloroethylene	8.5
	CO, CO <sub>2</sub>	5.7
	Total	99.9

## Example 12.

A "Pyrex" glass reactor having an inner diameter of 60 mm and a height of 500 mm and equipped with two blow pipes of glass (depth of liquid 10 cm) was charged with 339 cc of a molten salt composed of 10 mole% of chromic chloride and 90 mole% in total of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 7:3, and the molten salt was heated and maintained at 480°C. Then, into the molten salt were introduced 100 cc/min. of ethylene from one blow pipe and 100 cc/min. of hydrogen chloride and 125 cc/min. of air from the other pipe, and the oxychlorination of ethylene was performed continuously for 40 minutes. The effluent gas from the reactor was cooled to -30°C. The reaction product was collected, and analyzed. The conversion of ethylene was found to be about 100%, and the composition of the product was as shown in Table 15 below.

Table 15.

	<i>Product</i>	<i>Weight %</i>
60	Monochloroethylene	40.5
	1,2-Dichloroethane	2.2
	1,2- <i>cis</i> -Dichloroethylene	15.4
	1,2- <i>trans</i> -Dichloroethylene	7.2
	1,1-Dichloroethylene	3.1
	Trichloroethylene	14.0
65	1,1,2-Trichloroethane	1.7
	Tetrachloroethylene	14.9
	Tetrachloromethane	1.0
	Total	100.0

## Example 13.

The same reactor as used in Example 12 was charged with 339 cc of a molten salt catalyst composed of 7 mole% of nickel chloride and 93 mole%, in total, of cuprous chloride, cupric chloride and potassium chloride, the mole ratio of the copper chloride to potassium chloride being 6:4, and heated to 510°C. Then, into the molten salt were introduced 45 cc/min. of methane from one blow pipe and 180 cc/min. of hydrogen chloride and 225 cc/min. of air from the other blow pipe, and the oxychlorination of methane was performed continuously for 40 minutes. The effluent gas from the reactor was cooled to -10°C. The reaction product was collected, and analyzed. The conversion of methane was found to be about 100%, and the composition of the product was as shown in Table 16.

Table 16.

	<i>Product</i>	<i>Weight %</i>
75	Trichloromethane	1.1
	Tetrachloromethane	92.7
	Trichloroethylene	1.2
	Tetrachloroethylene	5.0
	Total	100.0

When the above procedure was repeated except using 3 mole% of nickel chloride and a 4 mole% of manganese chloride instead of 7 mole% of nickel chloride, the conversion of methane was about 100% and the composition of the product was almost the same as above.

Example 14.

The oxychlorination of propane was performed in the same way as set forth in Example 12 except that there was used a molten salt catalyst composed of 5 mole% of nickel chloride, 5 mole% of ferric chloride, 36 mole% of potassium chloride and 54 mole%, in total, of cuprous chloride and cupric chloride, the temperature of the molten salt was maintained at 500°C, and 50 cc/min. of propane, 400 cc/min. of hydrogen chloride and 1000 cc/min. of air were fed into the reactor. The reaction product was collected, and analyzed. The conversion of propane was found to be about 100%, and the composition of the product was as shown in Table 17.

Table 17.

	Product	Weight %
25	Monochloroethylene	trace
	1,2-cis-Dichloroethylene	0.2
	1,2-trans-Dichloroethylene	0.1
30	1,1-Dichloroethylene	trace
	Tetrachloromethane	29.6
	Trichloroethylene	8.3
	Tetrachloroethylene	61.7
	Total	99.9

Example 15.

The oxychlorination of propylene was performed in the same way as set forth in Example 14 except that there was used a molten salt catalyst composed of 4 mole% of

chromium chloride, 4 mole% of palladium chloride, 55 mole%, in total, of cuprous chloride and cupric chloride, and 37 mole% of potassium chloride, and the temperature of the molten salt was maintained at 490°C. The reaction product was collected, and analyzed. The conversion of propylene was found to be about 100%. The composition of the product was as shown in Table 18.

Table 18.

Product	Weight %	
Monochloroethylene	0.1	50
1,2-cis-Dichloroethylene	0.1	
Tetrachloromethane	35.7	
Trichloroethylene	7.4	
Tetrachloroethylene	56.7	
Total	100.0	55

Examples 16 to 19.

A quartz reactor having an inner diameter of 50 mm and a height of 800 mm and equipped with two blow pipes was charged with a molten salt catalyst of the composition indicated in Table 19, and the catalyst was maintained at a temperature indicated in Table 19. Then, into the molten salt were introduced benzene in the gaseous state and nitrogen from one pipe and hydrogen chloride and air from the other pipe, and the oxychlorination of benzene was performed continuously for one hour. The reaction conditions and the results obtained are shown in Table 19 below.

For comparison, the Example 16 procedure was repeated except that a molten salt composed of 40 mole% of potassium chloride and 60 mole%, in total, of cuprous chloride and cupric chloride was used. The conversion of benzene was found to be 18%.

TABLE 19

Example Nos.

Reaction Condition	16	17	18	19
Composition of the Molten Salt (mole%)	MnCl <sub>2</sub> 15	same as in Example 16	NdCl <sub>3</sub> 1	PdCl <sub>2</sub> 1
	KCl 34		FeCl <sub>3</sub> 14	FeCl 14
	CuCl <sub>2</sub> + CuCl 51		KCl 34	KCl 34
			CuCl <sub>2</sub> + CuCl 51	CuCl <sub>2</sub> + CuCl 51
Temperature (°C)	500	400	500	500

TABLE 19 (continued)

Reaction Condition	Example Nos.			
	16	17	18	19
<u>Feed Stock</u>				
Benzene (mole/hr.)	0.254	0.233	0.264	0.257
Hydrogen Chloride (litres/hr.)	18	18	18	18
Air (litre/hr.)	45	45	45	45
<u>Conversion of Benzene (%)</u>				
	45	6	68	64
<u>Composition of Product (Wt. %)</u>				
Monochlorobenzene	68.4	96.7	70.5	64.8
Dichlorobenzene	8.6	1.1	14.7	18.3
Trichlorobenzene	7.3	0.7	9.2	8.5
Tetrachlorobenzene	5.1	0.3	1.4	2.2
Diphenyl	7.5	1.1	3.1	4.5
Pentachlorobenzene	3.0	very small amount	0.7	0.8
Hexachlorobenzene	0.1	—	0.4	0.9

## Examples 20 to 21

The oxychlorination of toluene was performed in the same way as set forth in Example 16. The reaction conditions and the results obtained are given in Table 20 below. For comparison, the Example 21 procedure

was repeated except that there was used a molten salt catalyst composed of 40 mole% of potassium chloride and 60 mole%, in total, of cuprous chloride and cupric chloride. The conversion of toluene was found to be 5%. 10

TABLE 20

Reaction Composition	Example Nos.	
	20	21
Composition of the Molten Salt (mole%)	CrCl <sub>3</sub> 10 KCl 27 CuCl <sub>2</sub> 63 + CuCl	NdCl <sub>3</sub> 1 FeCl <sub>3</sub> 14 KCl 34 CuCl <sub>2</sub> 51 + CuCl
Temperature (°C)	480	350
Feed Stock		
Toluene (mole/hr.)	0.177	0.159
Hydrogen Chloride (litre/hr.)	6	6
Air (litre/hr.)	15	15
Conversion of toluene (%)	83	42
Composition of Product (wt.%)		
ClC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	47.4	72.8
Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>3</sub>	2.4	3.4
ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	1.3	—
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	19.6	1.5
C <sub>6</sub> H <sub>5</sub> CHCl <sub>2</sub>	9.3	11.6
C <sub>6</sub> H <sub>5</sub> CCl <sub>3</sub>	8.5	5.2
Others	11.5	5.5

## WHAT WE CLAIM IS:—

1. A process for preparing chlorinated hydrocarbons, which comprises oxychlorinating a starting hydrocarbon as herein defined with oxygen and chlorine and/or hydrogen chloride by contacting the reactants with a molten salt catalyst at a temperature of from 250 to 650°C, said catalyst comprising the following components to a total of 100%: (1) from 95 to 50 mole % of copper chloride as herein defined or a mixture of copper chloride and of an alkali metal chloride and/or an alkaline earth metal chloride, and (2) from 5 to 50 mole % of at least one chloride of a metal selected from iron, manganese,

chromium, nickel, palladium and the rare earth metals.

2. A process as claimed in claim 1, wherein the catalyst comprises from 93 to 60 mole % of the component (1) and from 7 to 40 mole % of the component (2).

3. A process as claimed in claim 1 or 2, wherein the molar proportion of alkali metal chloride and/or alkaline earth metal chloride to copper chloride in the component (1) does not exceed 2 : 1.

4. A process as claimed in claim 3, wherein said proportion does not exceed 1 : 1.

5. A process as claimed in any preceding claim, wherein the chlorine source is used in

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- an amount of from 0.1 to 20 moles, calculated as  $\text{Cl}_2$ , per mole of starting hydrocarbon.
6. A process as claimed in any preceding claim, wherein air is used as the source of oxygen.
7. A process as claimed in any preceding claim, wherein the oxygen is used in an amount of from 0.05 to 2 moles per mole of chlorine or hydrogen chloride.
- 10 8. A process as claimed in any preceding claim, wherein said alkali metal chloride is lithium chloride, sodium chloride or potassium chloride.
- 15 9. A process as claimed in any preceding claim, wherein said alkaline earth metal chloride is magnesium chloride.
10. A process as claimed in any preceding claim, wherein the chlorides of the rare earth metals are lanthanum chloride, cerium chloride, praseodymium chloride and neodymium chloride.
- 20 11. A process as claimed in any preceding claim, wherein the starting hydrocarbon is an aliphatic hydrocarbon having from 1 to 4 carbon atoms.
12. A process as claimed in any of claims 1 to 10, wherein the starting hydrocarbon is an aromatic hydrocarbon.
13. A process for preparing chlorinated hydrocarbon as claimed in claim 1 and substantially as herein described.
14. A process for preparing chlorinated hydrocarbons, substantially as herein described with reference to any one of the foregoing Examples of the invention.
- 30 15. Chlorinated hydrocarbons when prepared by a process as claimed in any preceding claim.

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